

**Laboratory Investigations in Support of Carbon Dioxide-Limestone Sequestration  
in the Ocean**

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### ABSTRACT

Research under this Project has proven that liquid carbon dioxide can be emulsified in water by using very fine particles as emulsion stabilizers. Hydrophilic particles stabilize a CO<sub>2</sub>-in-H<sub>2</sub>O (C/W) emulsion; hydrophobic particles stabilize a H<sub>2</sub>O-in-CO<sub>2</sub> (W/C) emulsion. The C/W emulsion consists of tiny CO<sub>2</sub> droplets coated with hydrophilic particles dispersed in water. The W/C emulsion consists of tiny H<sub>2</sub>O droplets coated with hydrophobic particles dispersed in liquid carbon dioxide. The coated droplets are called globules. The emulsions could be used for deep ocean sequestration of CO<sub>2</sub>. Liquid CO<sub>2</sub> is sparsely soluble in water, and is less dense than seawater. If neat, liquid CO<sub>2</sub> were injected in the deep ocean, it is likely that the dispersed CO<sub>2</sub> droplets would buoy upward and flash into vapor before the droplets dissolve in seawater. The resulting vapor bubbles would re-emerge into the atmosphere. On the other hand, the emulsion is denser than seawater, hence the emulsion plume would sink toward greater depth from the injection point.

For ocean sequestration a C/W emulsion appears to be most practical using limestone (CaCO<sub>3</sub>) particles of a few to ten μm diameter as stabilizing agents. A mix of one volume of liquid CO<sub>2</sub> with two volumes of H<sub>2</sub>O, plus 0.5 weight of pulverized limestone per weight of liquid CO<sub>2</sub> forms a stable emulsion with density 1087 kg m<sup>-3</sup>. Ambient seawater at 500 m depth has a density of approximately 1026 kg m<sup>-3</sup>, so the emulsion plume would sink by gravity while entraining ambient seawater till density equilibrium is reached.

Limestone is abundant world-wide, and is relatively cheap. Furthermore, upon disintegration of the emulsion the CaCO<sub>3</sub> particles would partially buffer the carbonic acid that forms when CO<sub>2</sub> dissolves in seawater, alleviating some of the concerns of discharging CO<sub>2</sub> in the deep ocean. Laboratory experiments showed that the CaCO<sub>3</sub> emulsion is slightly alkaline, not acidic.

We tested the release of the CO<sub>2</sub>-in-H<sub>2</sub>O emulsion stabilized by pulverized limestone in the DOE National Energy Technology Laboratory High Pressure Water Tunnel Facility (HPWTF). Digital photographs showed the sinking globules in the HPWTF, confirming the concept of releasing the emulsion in the deep ocean. We modeled the release of an emulsion from the CO<sub>2</sub> output of a 1000 MW coal-fired power plant at 500 m depth. The emulsion would typically sink several hundred meters before density equilibration with ambient seawater. The CO<sub>2</sub> globules would rain out from the equilibrated plume toward the ocean bottom where they would disintegrate due to wave action and bottom friction. Conceptual release systems are described both for an open ocean release and a sloping seabed release of the emulsion.

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## 1. INTRODUCTION

Deep ocean sequestration of the greenhouse gas CO<sub>2</sub> engenders strong opposition from environmental groups, marine biologists and others, because massive releases of liquid CO<sub>2</sub> at depth may acidify the surrounding seawater. When liquid CO<sub>2</sub> dissolves in seawater, carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is formed, which may harm aquatic organisms (1). Also, it is necessary to inject the liquid CO<sub>2</sub> as deep as possible in order to prolong its sequestration time (2). Several methods have been proposed to mitigate the acidification problem and to make the injected CO<sub>2</sub> plume sink further from the release point. (a) The release of pre-cooled, liquid CO<sub>2</sub>. Cold, liquid CO<sub>2</sub> is denser than seawater, making it sink deeper from the release point while entraining ambient seawater, thus diluting the carbonic acid formed (3). (b) The release of a mixture of cold, liquid CO<sub>2</sub> and cold seawater. This mixture forms a solid hydrate (CO<sub>2</sub>·6H<sub>2</sub>O) that is negatively buoyant and hinders the dissolution of CO<sub>2</sub> (4, 5). (c) The release of liquid CO<sub>2</sub> into a cylindrical open-ended vessel. This creates a dense plume that sinks further from the open bottom of the vessel while entraining ambient seawater, again diluting the carbonic acid formed (6). (d) The dispersion of liquid CO<sub>2</sub> droplets from a diffuser at the end of a pipe attached to a moving ship. This facilitates the dilution of the carbonic acid (7). (e) The release of a stoichiometric mixture of CO<sub>2</sub> and CaCO<sub>3</sub> in aqueous solution. The resulting solution of calcium and bicarbonate ions would not acidify the seawater around the injection point (8).

In this Project, we developed a different approach to deep ocean sequestration of CO<sub>2</sub>. We discovered that when liquid carbon dioxide, liquid water, and finely pulverized materials are mixed together under high pressure, a stable emulsion is formed in which the liquids do not separate. Oil-in-water (O/W) and water-in-oil (W/O) emulsions stabilized by fine particles were recently reviewed by Binks (9). However, to the best of our knowledge, liquid carbon dioxide-in-water (C/W) and water-in-liquid carbon dioxide (W/C) emulsions stabilized by fine particles were not reported before in the literature. Hydrophilic particles stabilize a C/W emulsion; hydrophobic particles stabilize a W/C emulsion. The C/W emulsion consists of tiny CO<sub>2</sub> droplets coated with hydrophilic particles dispersed in water. The W/C emulsion consists of tiny H<sub>2</sub>O droplets coated with hydrophobic particles dispersed in liquid carbon dioxide. Several hydrophilic particles were used to form a stable C/W emulsion, including pulverized limestone (CaCO<sub>3</sub>), pulverized sand (mainly SiO<sub>2</sub>), flyash as obtained from a local coal-fired power plant, pulverized shalestone, and pulverized lizardite (magnesium silicate). Also several hydrophobic particles were used to form a stable W/C emulsion, including pulverized Teflon, activated carbon, carbon black, and pulverized coal. The characteristics of the particles and the ensuing emulsions were described in detail in preceding semi-annual technical reports and in a major peer-reviewed journal article (10).

In this Final Report we concentrate on the emulsion that seems to be most suitable for deep ocean sequestration of CO<sub>2</sub>, namely a C/W emulsion which is formed when liquid carbon dioxide, liquid water and pulverized limestone (CaCO<sub>3</sub>) are mixed under high pressure. A practical mixing apparatus is described for the formation of the emulsion, as well as systems for an open ocean release and a sloping seabed release of the emulsion. The modeling of the transport and fate of the emulsion upon release in the deep ocean is described.

## 2. LIQUID CO<sub>2</sub>-H<sub>2</sub>O EMULSION

Water (polar) and carbon dioxide (non-polar) are very sparingly miscible in each other – solubility about 4.4% by weight of liquid CO<sub>2</sub> in water at 4.5 MPa, 15 °C (11). When mixed together the two liquids form two separate phases with a sharp meniscus between them. However, when the two liquids are mixed in the presence of finely dispersed hydrophilic particles that act as emulsifiers, the mixture forms a stable emulsion with water as the continuous phase and liquid carbon dioxide as the dispersed phase. The solid particles form a sheath around the CO<sub>2</sub> droplets, and because the particles are hydrophilic, they have greater surface area in contact with the continuous aqueous phase (9). The presence of the particle sheath provides a hindrance to coalescence of the carbon dioxide droplets. Thus, no phase separation occurs.

## 3. EXPERIMENTAL

### 3.1 Materials

**Carbon Dioxide.** Industrial grade liquid carbon dioxide was supplied from 50 lb syphon cylinders (Northeast Airgas).

**Water.** Water was either de-ionized and filtered in a laboratory system (Millipore Milli-RO), municipal tap water, or artificial seawater (3.5% by weight reagent grade NaCl). It is important to stress that artificial seawater does form stable emulsions with liquid CO<sub>2</sub> stabilized by fine particles, thus in actual large scale ocean releases of the emulsion there is no need to use de-ionized water.

**Limestone.** Mined pulverized limestone (96.5% CaCO<sub>3</sub>, 2% MgCO<sub>3</sub>, 1% silica and silicates, 0.5% others) supplied by Huber Engineered Materials, Quincy, IL, was used having a bulk specific gravity of 2.7 and a solubility of 0.0035 g/100 mL H<sub>2</sub>O at 100°C. The pulverized samples can be purchased with different size distributions. In these experiments mostly Hubercarb<sup>TM</sup> Q6 pulverized limestone with nominal median particle size of 6 μm was used. A scanning electron microscope (SEM) image of sample Q6 is shown in Figure 1. It can be seen that some particles are crystalline (rhombohedral), others are irregular. For large scale ocean sequestration it may be more economical to buy bulk limestone delivered to the sequestration site, and pulverizing it in commercial ball mills similar to those used to pulverize bulk coal for coal-fired power plants.

### 3.2 Mixing Apparatus

**High Pressure Batch Reactor.** The high pressure batch reactor (HPBR) used for creating a CO<sub>2</sub>-in-H<sub>2</sub>O emulsion stabilized by pulverized limestone particles is presented in Figure 2. The reactor consists of a stainless steel pressure cell of 85 mL internal volume equipped with tempered glass windows (PresSure Products G03XC01B). The windows are placed 180 degrees apart, one illuminated with a 20W 12V compact halogen bulb, the other allowing observation with a video camera. The view window diameter is 25 mm. The window diameter is used as a scale for determining droplet and globule diameter sizes. The reactor is equipped with a pressure relief valve (Swagelok R3-A),

thermocouple (Omega KMQSS-125G-6), pressure gauge (Swagelok PGI-63B), bleed valve (Swagelok SS-BVM2), and a 3.2 mm port for admitting CO<sub>2</sub>. A cylindrical magnetic stir bar with a cross shape on top (VWR Spinplus) is utilized for internal mixing. The stir bar rotated at 1300 RPM. Reactor temperature was adjusted by application of hot air from a heat gun, or solid dry ice chips.

The emulsion was prepared by adding a measured volume of CaCO<sub>3</sub> slurry in water through an opening of the HPBR, closing the opening, then adding a measured volume of liquid CO<sub>2</sub> by means of a syringe pump. The proportions of the ingredients were as follows: 10 g of particulate matter suspended in 65 mL water, 18 – 20 mL liquid CO<sub>2</sub>. The pressure in the HPBR was 17.2 MPa, temperature 15°C.

**High Pressure Flow Reactor.** For continuous mixing of the emulsion ingredients we used a high pressure flow reactor with a Kenics-type static mixer. The laboratory set-up is depicted in Figure 3. The static mixer is Koflow ¼-27, 0.63 cm internal diameter, 23.5 cm length with 27 baffles. A CaCO<sub>3</sub>/water slurry is prepared in a reservoir. Calcium carbonate particle sedimentation in the slurry is prevented by using constant recirculation with a pump. The slurry is pumped (Wanner Engineering D04-S) to 10 MPa through a double pipe heat exchanger, where it is cooled to 5-10 °C, into a mixing tee upstream of the static mixer. Compressed liquid CO<sub>2</sub> from a syringe pump (Isco 500D) at 10 MPa is co-injected into the static mixer. The two fluids are thoroughly mixed in the static mixer, and then flow into the view cell (Jerguson T32-11) in a downward flow. A quarter turn ball valve downstream of the cell may be closed to stagnate the emulsion for observation. The outlet of the cell is throttled through a back-pressure regulator (Tescom 54-2162) and the gas is vented. A 35 W halogen lamp with a parabolic reflector is used for illumination through one of the cell windows. A mat reflector is used on the opposite window for reflecting the illumination. Photographs are taken through the same cell window where the illuminating lamp is mounted. A fast frame video camera is used (Olympus C-730UZ) either mounted directly on the window of the cell, or looking through a 40x stereomicroscope (Leitz).

### 3.3 High Pressure Water Tunnel Facility

The NETL High Pressure Water Tunnel Facility (HPWTF) was used for simulating the release of the emulsion into the deep ocean. The HPWTF is described in detail by Haljasmaa et al. (12). The static mixer was adapted to the HPWTF as shown in Figure 4. Total liquid volume of the HPWTF comprises approximately 16.5 L. The HPWTF was evacuated, filled with reverse osmosis or artificial seawater, and brought to operating pressure (6.8 MPa) and temperature (4, 8 or 12 °C). The flow rate of water to the static mixer was controlled by varying the speed and hence dynamic pressure of the centrifugal pump and measured by an ultrasonic flow meter (Controlotron 1010FT). Flow rates are controllable between 0 and 1.9 L/min. A paste of 0.5 g/mL CaCO<sub>3</sub> was loaded into a high pressure syringe pump (Isco 500D) with a maximum delivery rate of 170 mL/min. Liquid CO<sub>2</sub> of 99.99% purity was loaded into a high pressure syringe pump (Isco 260D) with a maximum delivery rate of 100 mL/min. The observation section of the HPWTF is instrumented with 3 cameras, one digital camera on the upper oblong window, and two analog cameras on the upper and lower bull's eye windows, which recorded the appearance of the emulsion plume ensuing from the static mixer tube. The static mixer

device was operated in short intervals at varying proportions and flow rates. The outflow from the static mixer was stopped to observe the sinking or rising behavior of the emulsion plume in the HPWTF.

## 4. RESULTS

### 4.1 High Pressure Batch Reactor Results

Figure 5 shows the emulsion obtained when a slurry of Hubercarb Q6 limestone particles in de-ionized water are mixed with liquid CO<sub>2</sub> in the HPBR. After thorough mixing with the magnetic stir bar, most globules settled in the bottom of the pressure cell, indicating that the globules are heavier than the surrounding water. The globule diameter is in the 200 – 300 μm range.

Limestone particle stabilized macro-emulsions were also formed with a slurry of CaCO<sub>3</sub> particles in artificial seawater (a solution of 3.5% by weight NaCl in de-ionized water). The globule diameter is similar to that formed in de-ionized water alone, and all the initially present liquid CO<sub>2</sub> was emulsified. This experiment indicates that, for large scale CO<sub>2</sub> sequestration in the deep ocean, seawater can be used to form the emulsion instead of purified water.

In one run bromophenol blue indicator was added to the mix. The indicator turned from blue to yellow, indicating that the emulsion is slightly alkaline (pH  $\approx$  4.6), not acidic. The alkaline reaction is probably due to excess CaCO<sub>3</sub> in the emulsion. Thus, it is expected that in deep ocean sequestration, the CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> emulsion plume will not acidify the surrounding seawater. Even though the amount of CaCO<sub>3</sub> in the emulsion is below the stoichiometric amount needed to completely neutralize all of the carbonic acid that could potentially form, the CaCO<sub>3</sub> particle sheath around each emulsion droplet slows the dissolution process preventing localized acidification before adequate mixing can take place (see below).

### 4.2 High Pressure Flow Reactor Results

The Kenics-type static mixer was fed with a slurry of 10 g/L CaCO<sub>3</sub> particles in artificial seawater and liquid CO<sub>2</sub>. The flow rates were 1.5 L/min slurry and 0.15 L/min liquid CO<sub>2</sub>, both at 10 MPa, at a temperature of 5-10 °C. Because of the white background of excess CaCO<sub>3</sub> particles and low resolution, no distinct globules were visible in the Jerguson cell. However, no phase separation of liquid CO<sub>2</sub> was noticeable, indicating that a stable emulsion was formed. When the emulsion was brought to rest in the Jerguson cell, the globules were clearly visible (Figure 6). The diameter of the globules is in the 70 – 100 μm range, which is much smaller than obtained in the HPBR. This result indicates that the static mixer exerts a greater shear force on the liquid CO<sub>2</sub>-H<sub>2</sub>O mix, producing smaller globules and a finer emulsion. Therefore, a static mixer is recommended for deep ocean sequestration of the CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> emulsion.

### 4.3. High Pressure Water Tunnel Results

For the experiments in the DOE/NETL HPWTF the static mixer was fed with three fluids: 1. CaCO<sub>3</sub> paste in water (~0.5 g/mL CaCO<sub>3</sub>) at a rate of 10 mL/min; 2. Water at a rate of 1 L/min; 3. Liquid CO<sub>2</sub> at a rate of 100 mL/min. The water in the HPWTF was kept at 12 °C and 6.8 MPa pressure. An emulsion plume was observed, consisting of droplets of liquid CO<sub>2</sub> coated with a sheath of CaCO<sub>3</sub> particles dispersed in water. Typical globule diameter was in the range 300 – 500 μm (Figure 7), larger than obtained in the laboratory flow reactor. We attribute the larger size to the mode of mixing of the fluids. In the laboratory flow reactor two fluids were mixed – a slurry of CaCO<sub>3</sub> particles in water and liquid CO<sub>2</sub> – whereas in the HPWTF three fluids were mixed: a paste of CaCO<sub>3</sub> particles in water, water, and liquid CO<sub>2</sub>. Also the flow rates and pressures were different in the laboratory vs. the HPWTF. Nevertheless, the ensuing globules in the HPWTF were heavier than ambient water, therefore they sank toward the bottom of the HPWTF. The settling velocity of the globules in the HPWTF is estimated at  $2.2 \times 10^{-3} \text{ m s}^{-1}$ .

## 5. MODELING OF THE EMULSION PLUME IN THE DEEP OCEAN

Although not called for in the initial Statement of Work, we thought it may be integral to this Project to model the transport and fate of the CO<sub>2</sub>-H<sub>2</sub>O-CaCO<sub>3</sub> emulsion if it were injected into the deep ocean. The model is described in detail by Golomb et al. (13). Here we give a brief review of the structure of the model and the results of the calculations.

The model assumes that an emulsion is released consisting of a volume ratio of liquid CO<sub>2</sub> to water of 1:2, and pulverized limestone in a ratio of 0.5 kg of particles per kg of liquid CO<sub>2</sub>. A monolayer of particles around the CO<sub>2</sub> droplets would require only 0.2 kg of particles per kg of liquid CO<sub>2</sub>, but it may be desirable to add excess limestone particles in order to ensure that the appropriate size particles are present in the polydisperse batch of ground CaCO<sub>3</sub>. Furthermore, excess CaCO<sub>3</sub> helps to buffer the carbonic acid that may be formed. For example Hubercarb Q6 with median particle diameter 6 μm could be used for emulsion stabilization. The density of seawater at 500 m depth is assumed to be 1026 kg m<sup>-3</sup>, liquid CO<sub>2</sub> 930 kg m<sup>-3</sup>, and the limestone particle bulk density 2700 kg m<sup>-3</sup>. The gross density of the emulsion is 1087 kg m<sup>-3</sup>, much greater than the density of ambient seawater. Therefore, the emulsion will sink by gravity to greater depth from the injection point until density equilibration with the stratified seawater is reached. Two mathematical models of plume behavior were developed, one describing a vertical plume released in the open ocean and the other describing a plume released on a sloping seabed.

### 5.1 Open Ocean Plume Model

It is assumed that the plume resulting from an open ocean emulsion release is symmetric about a vertical axis. Only steady (i.e., time-independent) plumes are considered. Three state variables are used: plume radius  $r$ , downward plume velocity  $u$ , and plume density  $\rho$  (Figure 8). All three quantities are taken to be average values over a horizontal plume cross-section, so all three depend only on depth  $z$ . The ambient seawater is assumed to be

at rest with known density profile  $\rho_a(z)$ . Pressure is assumed to be hydrostatic, and pressure in the plume at depth  $z$  is assumed equal to ambient pressure at the same depth. The effects of salinity and temperature variation are treated only through their combined effect on density. It is assumed that the plume entrains ambient seawater at a rate proportional to the plume velocity.

Conservation of mass, conservation of buoyancy, and the momentum equation take the form (14):

$$\frac{d}{dz} [r^2 u] = 2Eru \quad (1)$$

$$\frac{d}{dz} [r^2 u \rho] = 2Eru \rho_a \quad (2)$$

$$\frac{d}{dz} [r^2 u^2 \rho] = r^2 g (\rho - \rho_a) \quad (3)$$

Here  $E$  denotes the entrainment coefficient (assumed constant) and  $g$  denotes gravitational acceleration. Calculations are performed using two values of  $E$ : 0.05 and 0.1. These values were chosen to bracket the value  $E = 0.07$  used by Adams and coworkers (14). The values of the state variables are assumed known at the emulsion release depth  $z_0$ . The model equations are solved numerically using the MATLAB<sup>®</sup> routine *ode45*, an explicit, adaptive Runge-Kutta algorithm. The plume radius typically increases with depth, while plume velocity and density decrease with depth. The numerical integration is stopped when plume density reaches ambient density.

The quantity of greatest interest is the plume length, taken to be the difference between the depth at which plume becomes neutrally buoyant and the plume release depth. As will be seen below, the ambient density profile has a significant effect on plume length. Density stratification is measured by the buoyancy frequency  $N$ , defined as

$$N^2 = \frac{g}{\rho_{as}} \frac{d\rho_a}{dz} \quad (4)$$

where  $\rho_{as}$  is the seawater density at the ocean surface. In our model,  $N^2$  is taken to be a constant, corresponding to linear stratification, and the ambient seawater density  $\rho_{as}$  at the ocean surface is taken to be  $1026 \text{ kg m}^{-3}$ . A value of  $10^{-4}$  for  $N^2$  corresponds to a density stratification  $d\rho_a/dz$  of  $1.05 \times 10^{-2} \text{ kg m}^{-3}$  per meter, while a value of  $10^{-6}$  for  $N^2$  corresponds to a density stratification of  $1.05 \times 10^{-4} \text{ kg m}^{-3}$  per meter.

As mentioned above, the emulsion consists of liquid  $\text{CO}_2$ , ambient seawater and pulverized limestone. With the volume and mass ratios of the ingredients given above, the gross density of the emulsion at the exit of the delivery pipe is  $1087 \text{ kg m}^{-3}$ . Three fluxes of liquid  $\text{CO}_2$  are considered, 62.5, 125 and  $250 \text{ kg s}^{-1}$ , corresponding to the output of typical coal fired power plants of 250, 500 and 1000 MW electric power (15). The initial plume velocity equals the initial volume flux divided by the cross-sectional area of the delivery pipe, the radius of which is taken to be 0.5 m. For the three fluxes, the initial plume velocities are calculated as 0.279, 0.558 and  $1.12 \text{ m s}^{-1}$ , respectively.

In Figure 9 the plume length is plotted against buoyancy frequency for six sets of parameter values. In all cases, the release depth is taken to be 500 m. Note that plume

length increases as CO<sub>2</sub> flux increases and as stratification and entrainment coefficient decrease.

## 5.2 Sloping Seabed Plume Model

In the coastal release model, the plume is assumed to advance along a valley in the seabed, which is taken to be an inclined plane at angle  $\theta$  with the horizontal (Figure 10). The plume is assumed to have a semicircular cross section. The independent variable is taken to be distance  $\xi$  from the release point measured along the plume bottom centerline; state variables include plume radius  $r$ , plume velocity  $u$ , plume density  $\rho$ , and depth  $z$ .

The following model equations represent conservation of mass, conservation of buoyancy, the momentum equation along the plume bottom centerline, and the geometric relationship between depth  $z$  and seabed slope  $\theta$  (16).

$$\frac{d}{d\xi} [r^2 u] = E r u \quad (5)$$

$$\frac{d}{d\xi} [\rho r^2 u] = E r u \rho_a \quad (6)$$

$$\frac{d}{d\xi} [\rho r^2 u^2] = g r^2 (\rho - \rho_a) \sin \theta - 2 C_D r \rho u^2 / \pi \quad (7)$$

$$\frac{dz}{d\xi} = \sin \theta \quad (8)$$

Here  $E$  denotes the entrainment coefficient and  $C_D$  denotes the coefficient of friction (assumed constant) between the plume and the seabed. The entrainment coefficient for a plume on a sloping bed is not constant but depends on the Richardson number  $Ri = g r (\rho - \rho_a) \cos(\theta) / (\rho u^2)$  (17). The following two experimentally determined formulas for the entrainment coefficient are used (18)

$$E = \begin{cases} 0.07 & \text{for } Ri < 10^{-2} \\ 0.07 Ri^{-1/2} & \text{for } 10^{-2} \leq Ri \leq 1 \\ 0.07 Ri^{-3/2} & \text{for } Ri > 1 \end{cases} \quad (9)$$

and

$$E = 0.002 Ri^{-1} \text{ for } 0.1 < Ri < 10 \quad (10)$$

Equation (9) is used outside the range of validity of (10). When both (9) and (10) are valid, the average of the two values is used.

The model equations (5) – (8) are solved numerically using the MATLAB<sup>®</sup> routine *ode45*, with integration stopping when plume density reaches ambient density. As in the open ocean model, the quantity of greatest interest is the vertical plume length, taken to be the difference between the depth at which plume becomes neutrally buoyant and the plume release depth. Figure 11 shows the dependence of vertical plume length on density stratification for two values of the friction coefficient and three values of the CO<sub>2</sub>

flux. In the set of curves on the left, the seabed slope is taken as  $1^\circ$ , while on the right the slope is taken as  $10^\circ$ . In all cases, the initial plume direction is directly downslope. Note that vertical plume length increases with decreasing stratification, with increasing seabed slope, and with increasing friction coefficient. Plumes on sloping seabeds are longer than vertical plumes in the open ocean because the entrainment rate is lower. Less plume surface area is exposed to the ambient seawater for a plume on a sloping seabed. Furthermore, friction with the seabed slows the plume velocity, further decreasing the entrainment rate (because entrainment rate is proportional to plume velocity).

## 6. RELEASE SYSTEMS

We present here conceptual release systems for large scale injection of the  $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$  emulsion. An open ocean and a continental slope release system are described. Both systems involve a Kenics-type static mixer, which our laboratory experiments showed to be efficient and economic for creating large quantities of the emulsion in a continuous fashion.

### 6.1 Open Ocean Release System

For injection of the emulsion into the open ocean, we visualize a system depicted in Figure 12. A floating platform is tethered to the ocean bottom. Liquid  $\text{CO}_2$  is barged to the platform and stored in a tank. Pulverized limestone is barged to the platform and slurried with seawater pumped from a depth of about 200 m (below the photic zone). The liquid  $\text{CO}_2$  and limestone slurry are piped to a depth of about 500 m into a static mixer. Before entering the mixer the limestone slurry is diluted by ambient seawater, which is drawn by aspiration. As noted above, the mix ensuing from the static mixer has a gross density of  $1087 \text{ kg m}^{-3}$ . The only power requirements for creating the mix are for pumping seawater from a depth of 200 m into the slurry mixer, and the mechanical mixing of the slurry. No additional power is required for the undersea static mixer; the hydrostatic pressures of the liquid  $\text{CO}_2$  and the pulverized limestone slurry provide adequate force for mixing the ingredients in the static mixer.

### 6.2 Sloping Seabed Release System.

When a depth of about 500 m can be reached within 100 – 200 km from shore, a pipe system laid on the continental slope may be more economic than delivering the ingredients of the emulsion to a floating platform by barges. The system is depicted in Figure 13. Liquid  $\text{CO}_2$  is stored on-shore in a tank. A slurry of pulverized limestone in seawater is prepared on-shore. The seawater for the slurry is pumped from about 200 m below the surface. Liquid  $\text{CO}_2$  is pumped from the tank into a pipe, where it flows to a depth of about 500 m, then into the static mixer. The limestone slurry is diluted with ambient seawater by aspiration before it flows into the static mixer. The mixer lies on the bottom slope. The proportion of the ingredients is the same as in the open ocean release.

## 7. ULTIMATE FATE OF THE EMULSION

The above modeling studies show that the dense plume comes to a rest when sufficient ambient seawater is entrained, so that its density asymptotically reaches the density of the ambient seawater. The question of what happens to the globules, *i.e.*, the ultimate fate of the liquid CO<sub>2</sub> droplets that are sheathed with fine limestone particles is of primary concern. Laboratory experiments showed that the globules are stable during observational periods of several hours (10). The experiments also showed that the globules are heavier than ambient water, for they settled in the bottom of the water-filled high pressure observation cell. Therefore, we postulate that after the plume comes to rest, the globules, together with excess pulverized limestone, will “rain-out” from the plume on their way to the ocean bottom. Using Stokes’ law for the settling of small particles in a viscous medium, we estimate that 100 μm radius globules sheathed with a 6 μm thick layer of limestone particles sink at a velocity of approximately  $2 \times 10^{-3} \text{ m s}^{-1}$ , that is, about 200 m d<sup>-1</sup>. Because the limestone particles are held by interfacial forces between the dispersed liquid CO<sub>2</sub> droplets and external seawater, it is unlikely that the sheath will rapidly dissolve during the fall to the ocean bottom. Eventually, the globules may disintegrate due to wave action and bottom friction. A part of the dissolved carbonic acid may be buffered by the CaCO<sub>3</sub> particles, according to the reaction:



The mix ensuing from the static mixer contains 0.5 g CaCO<sub>3</sub> per g of CO<sub>2</sub> compared to a stoichiometric ratio of 2.3 g CaCO<sub>3</sub> per g of CO<sub>2</sub>, not sufficient to completely buffer the carbonic acid. The rest of the dissolved carbonic acid may be dispersed and diluted over the ocean bottom. Further studies are warranted on the sensitivity of benthic organisms to diluted carbonic acid.

## 8. ECONOMICS

Huber Engineered Materials, Quincy, IL, sells pulverized limestone Q6 for \$38/t FOB. The median size of Q6 is 6 μm, its composition is 96.5% CaCO<sub>3</sub>, 2% MgCO<sub>3</sub>, 1% silica and silicates, and 0.5% others. Alternatively, raw limestone in chunks can be purchased from several quarries for \$5 –10/t FOB, and milled to the desired size on-site. In this case the major cost elements are the capital and operating costs of the grinding mills, resulting in a total cost of about \$13 per ton of pulverized limestone, including the cost of raw material and shipping. Because we need approximately 0.5 ton of pulverized limestone per ton of liquid CO<sub>2</sub>, the total cost of providing the pulverized limestone on site is about \$6.5 per ton of liquid CO<sub>2</sub>, not including the capital and operating cost of the slurry mixer, which may double the cost of preparing the slurry. Currently, the cost estimates of capturing and liquefying CO<sub>2</sub> at a coal-fired power plant range from \$15 to \$75/t CO<sub>2</sub> (20). Thus, the sequestration of liquid CO<sub>2</sub> in the form of an emulsion would add about 20% to 90% to the capture cost of CO<sub>2</sub>, excluding transport costs to the injection site. However, this additional cost may be justified on account of prolonging the sequestration period of the released CO<sub>2</sub>, and of not acidifying the seawater around the injection point.

## CONCLUSIONS

Deep ocean sequestration of carbon dioxide engenders several constraints: (a) ecological, because the injection of massive amounts of CO<sub>2</sub> would acidify significant volumes of seawater surrounding the injection point, which may be harmful to marine organisms; (b) technical, because the conveyance of liquid CO<sub>2</sub> to the deep ocean by pipeline or tanker requires complicated ocean engineering; (c) economical, because the transport and dispersion of liquid CO<sub>2</sub> in the deep ocean may add significantly to the sequestration cost; (d) legal, because most deep waters are international, and standing international regulations such as the 1972 London Convention on Ocean Dumping may not permit it.

The research under this Project showed that some, but not all, of the constraints may be alleviated by releasing an emulsion of liquid CO<sub>2</sub>-in-water stabilized by very fine pulverized limestone (CaCO<sub>3</sub>) particles. (a) The emulsion is denser than seawater, therefore the emulsion plume would sink deeper from the injection point, prolonging the sequestration period. (b) Because of the excess CaCO<sub>3</sub>, the emulsion would partially buffer the carbonic acid resulting from the dissolution of CO<sub>2</sub> in seawater. (c) Because of the sinking nature of the plume, the emulsion needs only to be conveyed to 500 m depth (the flash point of liquid CO<sub>2</sub> into vapor), reducing the transport cost of CO<sub>2</sub> to the deep ocean. However, the capital and operating cost of the emulsion mixing facility does add significantly to the sequestration cost of CO<sub>2</sub>. Furthermore, it is not clear whether the injection of the emulsion would be permitted under international law.

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## FIGURES

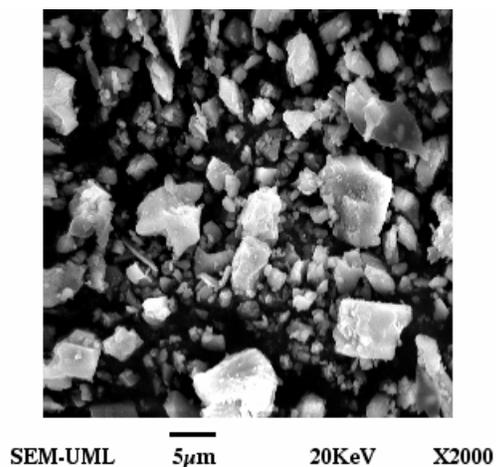


Fig. 1 Scanning Electron Micrograph (SEM) of Huber Engineered Materials Hubercarb Q6.

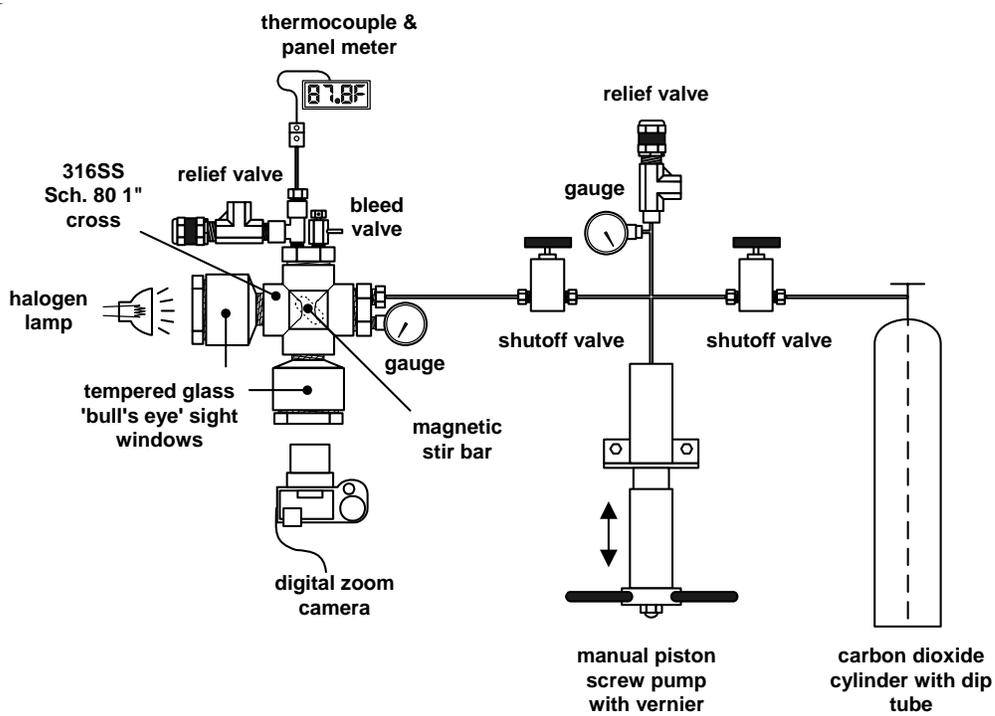


Fig. 2 Schematic of High Pressure Batch Reactor with Auxiliary Equipment



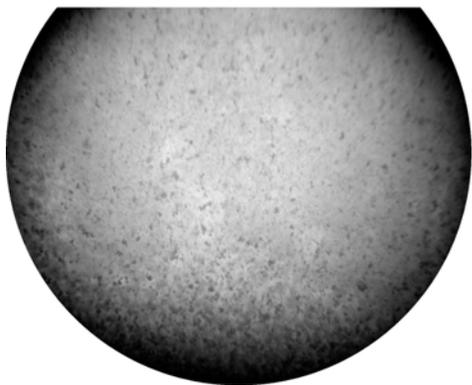


Fig. 5 Photo of Emulsion Stabilized with Hubercarb Q6 Pulverized Limestone in High Pressure Batch Reactor. Globule Diameter 200 – 300  $\mu\text{m}$

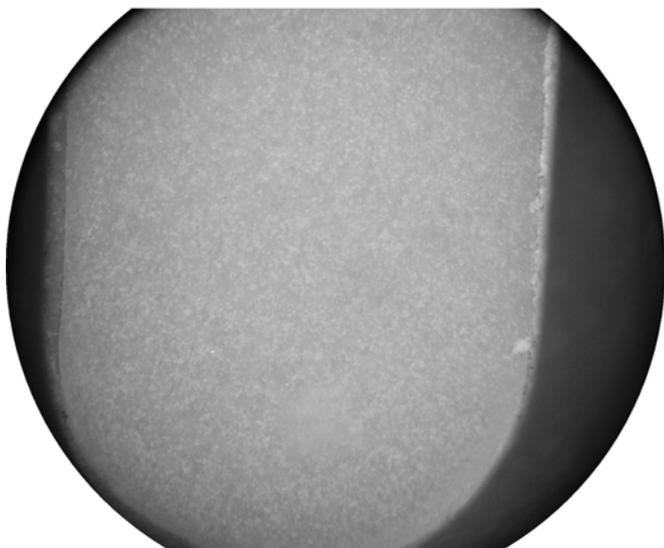


Fig. 6 Photo of Emulsion Ensuing from Kenics-type Static Mixer in the Laboratory. Globule Diameter 70 – 100  $\mu\text{m}$

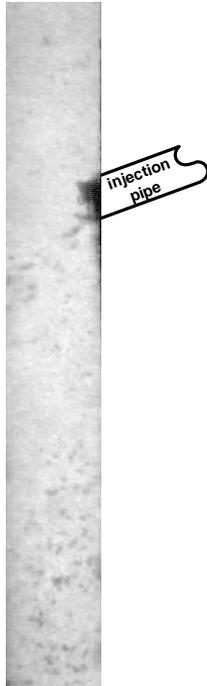


Fig. 7 Photo of Emulsion Ensuing from Kenics-type Static Mixer in HPWTF

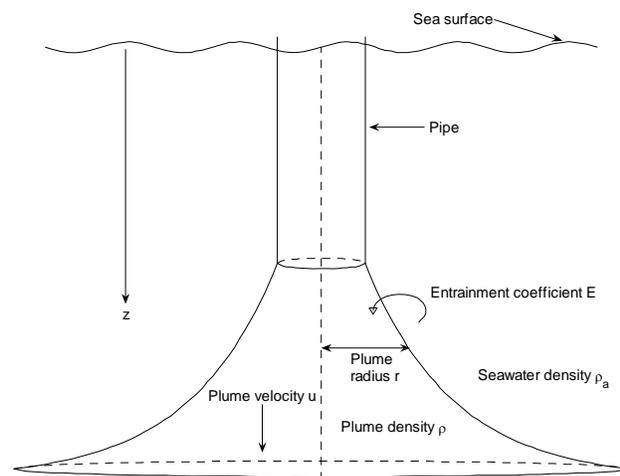


Fig. 8 Schematic of Open Ocean Emulsion Plume

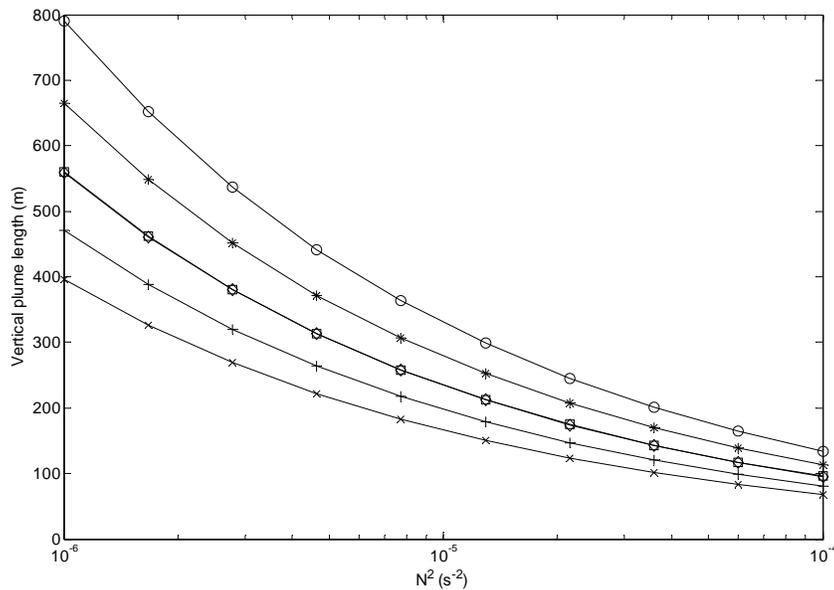


Fig. 9 Dependence of Plume Length on Density Stratification

Circle:  $E=0.05$ ;  $\text{CO}_2$  flux = 250 kg/s ( $u_0 = 1.12$  m/s)

Asterisk:  $E=0.05$ ;  $\text{CO}_2$  flux = 125 kg/s ( $u_0 = 0.558$  m/s)

Square:  $E=0.05$ ;  $\text{CO}_2$  flux = 62.5 kg/s ( $u_0 = 0.279$  m/s)

Diamond:  $E=0.1$ ;  $\text{CO}_2$  flux = 250 kg/s ( $u_0 = 1.12$  m/s)

Plus:  $E=0.1$ ;  $\text{CO}_2$  flux = 125 kg/s ( $u_0 = 0.558$  m/s)

Cross:  $E=0.1$ ;  $\text{CO}_2$  flux = 62.5 kg/s ( $u_0 = 0.279$  m/s)

A  $\text{CO}_2$  flux of 250 kg/s corresponds to an output of a 1000  $\text{MW}_{\text{el}}$  coal-fired power plant.

Note that the squares and diamonds overlap

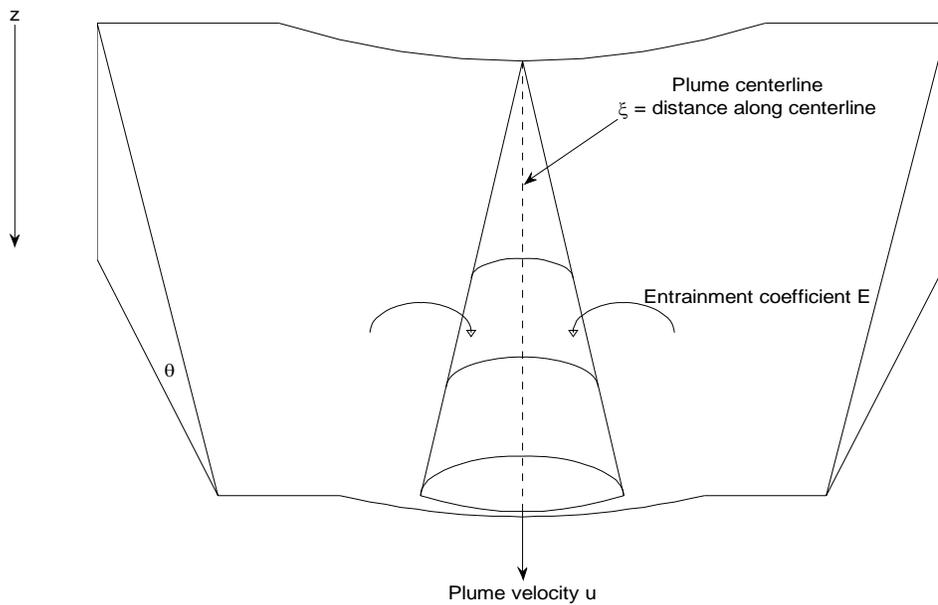


Fig. 10 Schematic of Sloping Seabed Emulsion Plume

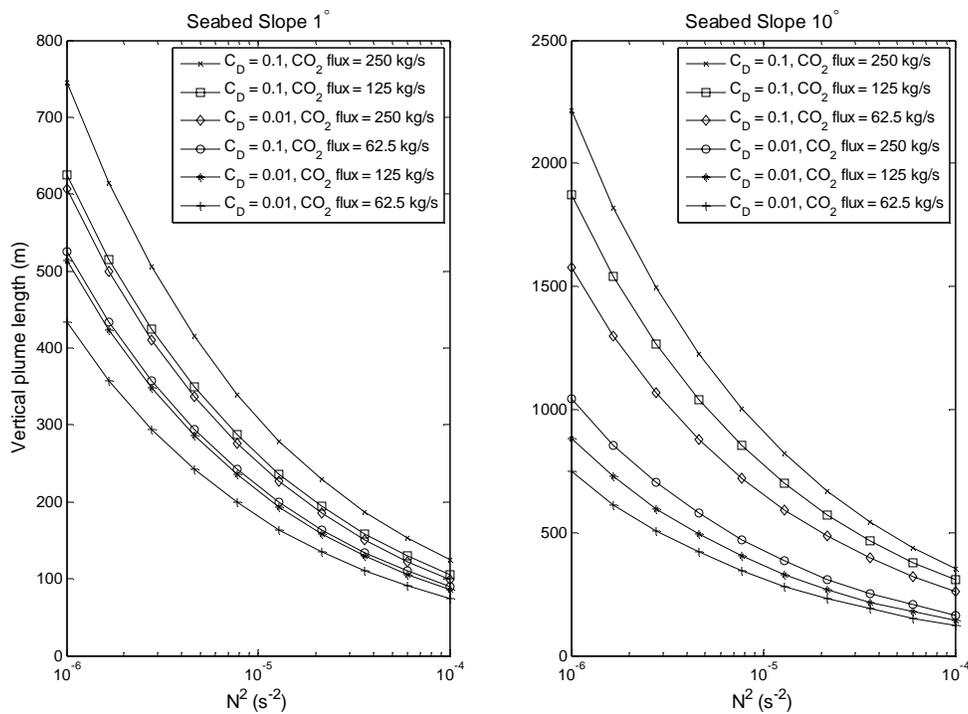


Fig. 11 Vertical Plume Length vs. Density Stratification for Seabed with Slope 1° (left) and 10° (right)

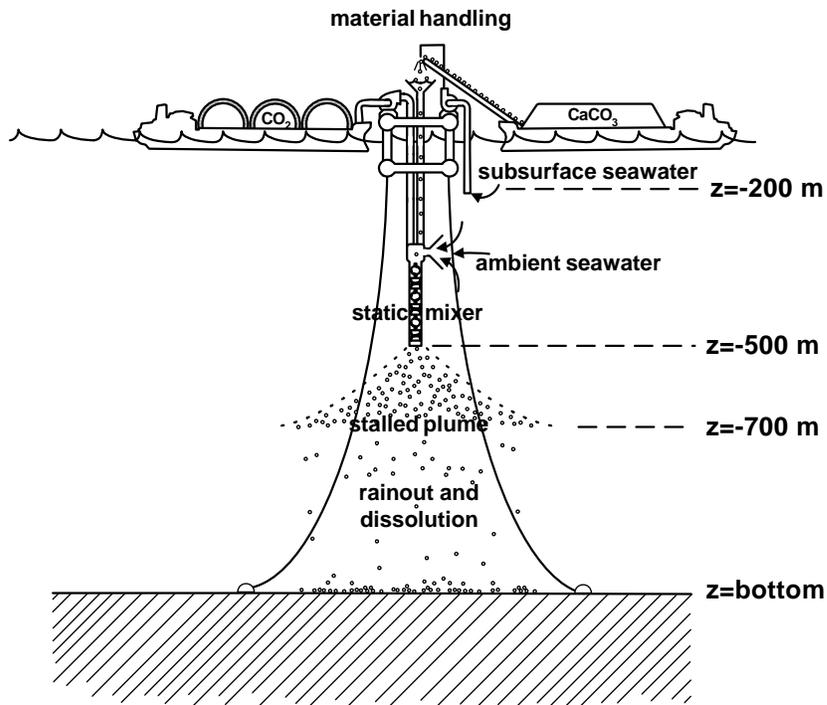


Fig. 12 Conceptual Open Ocean Release System

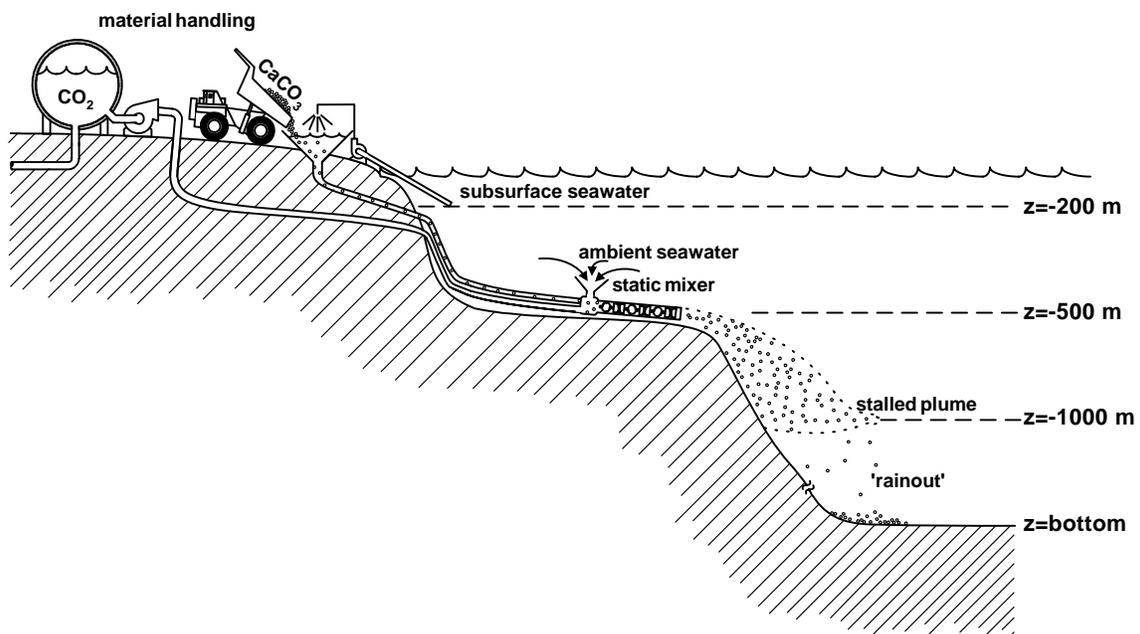


Fig. 13 Conceptual Sloping Seabed Release System